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Collector mixtures and their synergistic effect on quartz floatability

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Abstract

Sinergy is the interaction of two or more agents to produce a combined effect greater than the sum of their separate effects. Etherdiamine yields superior results for quartz floatability in a Hallimond tube and higher selectivity in the reverse bench scale cationic flotation of an iron ore, when compared to ethermonoamine. Blending these collectors yields better results than each one used individually characterizing a synergistic effect. This work evaluated the effects of the collectors ethermonoamine, etherdiamine and the mixture of these at the ratio 1:1 on the flotation of the quartz through the microflotation and bench flotation tests with a typical Brazilian iron ore. The results demonstrated the occurrence of synergistic effects in tests performed at concentrations of 1 and 3 mg/L and pH 10.5, in the absence of a depressant. In the presence of a depressant, the synergy was not observed under the same tested conditions, due to the collector-depressant interaction. On other hand, the bench flotation tests indicated the occurrence of synergy regarding silica content in the concentrate while an additive effect was observed for the iron recovery and Selectivity Index index demonstrating that a feasibility of using collector mixtures in this process, was not clearly achieved on the tested ratio 1:1.

keywords: etheramines, iron ore, synergistic effect, quartz microflotation.

1. Introduction

The analysis of the synergistic action of flotation reagents mixtures is complex and depends on the chemical interaction between the involved flotation reagents. Each reagent in a mixture may keep its chemical composition or mixing may result in a different species (Bradshaw *et al.*, 1998).

When the association of two or more products has the same effect as the vectorial sum of their individual effects, the effect is called additive. If this association impairs the effect, it is called antagonistic. The synergistic effect occurs when the combination of the products enhances the performance compared to the weighted sum of their individual effects. The identification of synergistic effects in reagent combinations on flotation results in the development of an innovative product or process.

Synergistic effects occur with all functional reagent applications, such as collectors, frother, (Dey *et al.*, 2014; McFadzean *et al.*, 2016; Nakhaei and Irannajad, 2017) and modifiers (Corin and Harris, 2010) in many ore flotation processes, such as sulfide ores, coal and silicate ores. The benefit of surfactant mixtures has been reported in several studies with anionic, cationic and non-ionic collectors (Bradshaw *et al.*, 1998; Filippov *et al.*, 2010; Hanumantha Rao *et al.*, 2011; Hao Jian *et al.*, 2017; Nakhaei and Irannajad, 2017).

A promising route in research related to froth flotation is the synergy in collector co-adsorption, whereas the same surface property is achieved with less reagent consumption, greater selectivity or metallic recovery (Hanumantha Rao *et al.*, 2011; Vidyadhar *et al.*, 2012).

Bradshaw *et al.*, (1998) stated that the addition of just one collector in a given flotation system can lead to adsorption only at strong sites, forming a non-uniform coverage and thus reducing the adsorption capacity. This is no longer observed in previously mixed collectors before their addition to the system, which indicates that synergism depends on the addition sequence as well as on the presence of a mixture.

According to Viana *et al.*, (2005), the mixture of different collectors often leads to the synergy of their effects on the properties of the investigated system. This fact is attributed to the impact that the mixture generates on the critical micellar concentration (CMC) and on the interfacial tension (IT), which are smaller than the CMC and IT of each reagent individually. These authors reviewed the main aspects of the collecting mixture in flotation and presented results of microflotation of some silicates in the presence of mixtures of anionic (sulfonate) and cationic (dodecylamine) collectors.

The use of a combination of weaker collectors with foaming properties and stronger collectors without foaming properties also shows a relevant increase in performance, as recovery of the fine particles and coarse particles increases. However, in this case, it is not a true synergistic effect, since the combined effect is the sum of the individual ones (Bradshaw *et al.*, 1998).

Investigations on the adsorption mechanism of mixtures of cationic amine C_{12} and anionic surfactants sulphate and oleate were performed by Vidyadhar *et al.*, (2012). The results indicated that the presence of oleate increased the adsorption of the C_{12} amine due to a decrease in the head-to-head electrostatic repulsion between the ammonium ions, adjacent to the mineral surface, increasing the tail-tail hydrophobic side interactions.

The most important collectors used in reverse cationic flotation of iron ores are etheramines. Studies of Matos *et al.*, (2021a) compared the effects of structural ethermonoamine and etherdiamine on selectivity of a typical Brazilian iron ore. Filippov *et al.*, (2010) studied the use of mixtures of etheramines with primary monoamines or alcohols in the reverse cationic flotation of a 3% SiO_2 magnetitic iron ore concentrate, where a hydrophobic layer was adsorbed on the surface of these aggregates causing the flotation of these complexes and yielding concentrates with SiO_2 content below 1% and iron content of 70.3%.

This article aims to evaluate the effects of a binary mixture of an ethermonoamine with an etherdiamine on quartz Hallimond tube floatability and on the selectivity of an iron ore bench flotation tests.

2. Materials and methods

Materials

Pure minerals and reagents

Samples of quartz collected at the Brazilian Iron Quadrangle were comminuted in porcelain mortar. Particles in the size range between 75μm and 150μm were selected by wet screening, under vibration, without chemical addition.

The evaluated cationic collectors were the commercial ethermonoamine (EDA3) and the etherdiamine (F2835-2) with 99% of purity, supplied by Clariant. The binary ratio of 1:1 (ethermonoamine:etherdiamine) was adopted for mixture tests. A cassava starch causticized solution was used as depressant, gelatinized at 5:1 starch:NaOH weight ratio.

The collector and depressant solutions used for microflotation and bench flotation tests were diluted to 0.1% and 1% (w/v), respectively, into 1000mL volumetric flasks. Sodium hydroxide (NaOH) and acetic acid (CH_3COOH) solutions were prepared at 1% (w/v) and used for pH control set as 10.5.

Methods

Samples characterization

The X-ray diffraction method (XRD) was used to check the purity degree of the quartz sample. The diffractometer model EMPYREAN from PANALYTICAL, with copper tube (CuKα radiation, with λ=1.5406 Å), was used to analyse the mineral sample in the size range < 400μm fraction. The results are shown in Figure 1.

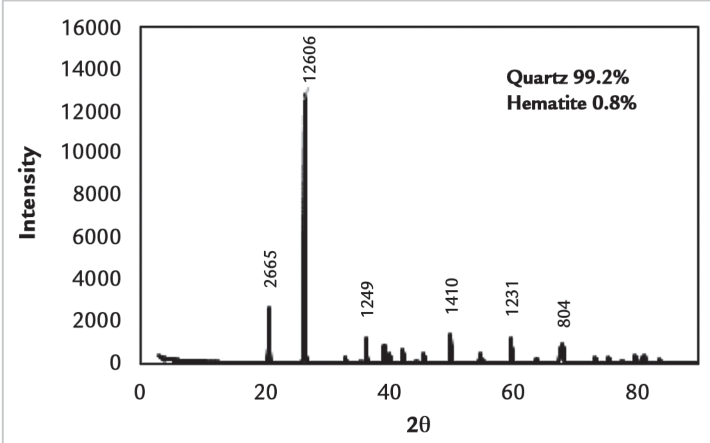

Figure 1 - X-ray diffraction of quartz.

The quantitative chemical analyses of the quartz and iron ore samples, performed by X-ray fluorescence spectrometry (RIGAKU apparatus) are presented in Tables 1 and 2, respectively.

Table 1 - Chemical composition of the quartz sample.

Percentage in the sample (%) – Quartz									
Fe	SiO_2	Al_2O_3	P	PPC	Mn	CaO	MgO	TiO_2	Total
0.57	98.90	0.14	0.003	0.05	0.00	0.00	0.09	0.00	100.00

Table 2 - Chemical composition of the iron ore.

Percentage in the sample (%) - Fe e SiO_2									
Fe	SiO_2	Al_2O_3	P	PPC	Mn	CaO	MgO	TiO_2	Total
44.82	33.40	0.21	0.028	2.12	0.065	0.005	0.04	0.00	100.00

Surface tension measurements

The DuNouy Ring method was used to determine the surface tension of the surfactants at room temperature (23°C ± 0.5°C). Triplicates were performed and averages were calculated for each point. The platinum ring was cleaned with ethanol and subsequently taken to a flame to remove any organic contaminants before each measurement.

Microflotation experiments

The microflotation tests were carried out in a modified Hallimond tube with a volume of 400mL. Each test was performed with 1g of the mineral sample. In tests using depressant solution, the mineral was initially conditioned for 5 minutes. The conditioning time of the collector and the flotation time was 1 min in each stage, following the procedure described by Matos *et al.*, (2019). Nitrogen gas (60mL/min) was used for generating bubbles. The floated and unfloated fractions were filtered, dried and weighed in the analytical balance model AUW220D / SHIMADZU (d = 0.1mg/0.01mg) to calculate the floatability.

Bench scale flotation tests

Standard procedures described by Matos (2017) were used to perform bench flotation experiments. An ore aliquot of 1500gr was used for each test, in a Wemco machine equipped with a 3.9L cell, to form 50% (w/w) solid feed pulp. The cassava starch and amine solution are added and conditioned at 1200rpm, during 3 and 1 minutes, respectively. The pulp is diluted to 42% solids for sequential flotation at constant air flow (4L/min), collection is made during 3 minutes, filtration, drying and weighing of tailings and concentrate were done for subsequent chemical analysis.

Design of Experiments (DOE)

The microflotation and bench flotation tests were conducted according to a full factorial design method at two experimental levels (upper and lower levels) and replicated responses. The following variables and their respective experimental levels were: (i) collector type (ethermonoamine and etherdiamine binary mixture 1:1); concentrations (1 and 3mg/L), for microflotation or the dosages (45 and 55g/t) for bench flotation. The matrix block of experiments adopted was randomized using the statistical software package Minitab® 18. The randomness of the tests allows the balance of the measurements and avoids possible mistakes in the evaluation of the results.

3. Results and discussion

Surface tension measurements

Figure 2 presents the surface tension results from etheramines and their binary mixture solutions. The results demonstrated that etherdiamine was more effective than ethermonoamine regarding surface tension reduction. Matos *et al*., (2021a) found similar results for analogous products. These authors justified these differences by the longer hydrocarbon chain of etherdiamine. The mixture of etheramines showed intermediate results characterizing addictive effects. Liu *et al*., (2020) performed surface tension measurements with cationic (DDA), anionic (sodium oleate and triethanolamine), and non-ionic (Tween and Span) surfactants, with their respective mixtures. In this study, the authors found synergistic effects for all the tested blends.

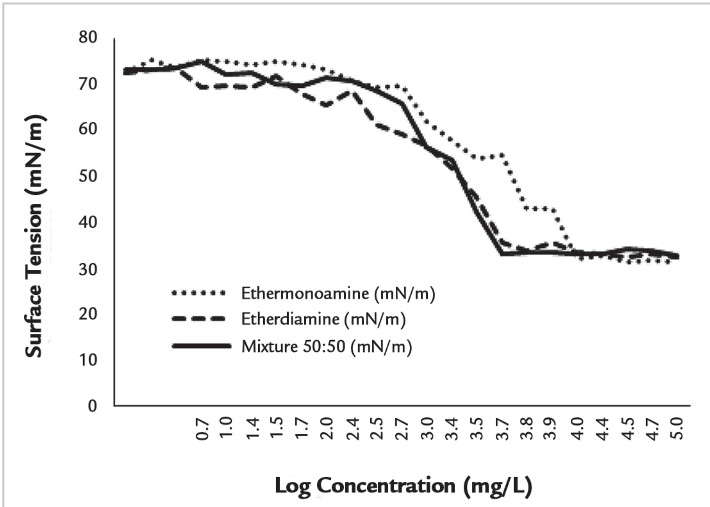

Figure 2 - Surface tension versus concentration of etheramines and their mixtures.

Figure 2 shows that the critical micelle concentration (CMC) of etherdiamine and mixture were approximately 5000 mg/L (logC = 3.7) for surface tension of 33.30 dyne/cm, while for ethermonoamine the CMC was approximately 10.000 mg/L (logC = 4.0) and surface tension of 33.33 dyne/cm. For this evaluation, the results showed that the mixture had an addictive effect.

Microflotation

The statistical significance of the factors and their interactions in the DOE were evaluated through a Pareto Chart. These analyses allow determining which factors and interactions have statistical significance and influence on the experimental responses, for 95% of statistical confidence grade. Figure 3 shows that both factors (collector concentration and type) and their interaction were significant for the evaluated response.

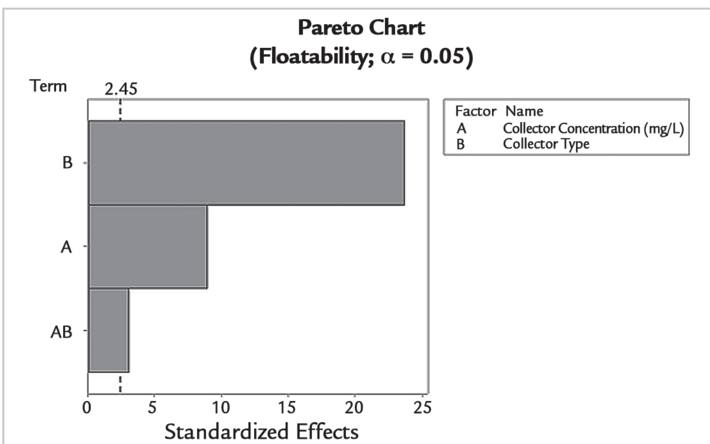

Figure 3 - Pareto plot of the standardized effects.

Effect of etheramines and their mixture in depressant absence

Normally, the increase in collector dosage enhances the quartz floatability, as shown by ethermonoamine in Figure 4. Etherdiamine yielded higher values of quartz floatability at 1 mg/L, replicating the results found by Matos *et al*., (2019). Surprisingly, the results also show that the binary mixture 1:1 produced higher quartz floatability than each etheramine individually, clearly demonstrating the synergistic effect occurrence. However, for etherdiamine and the mixture, the floatability at the concentration of 1 mg/L was higher than at 3mg/L.

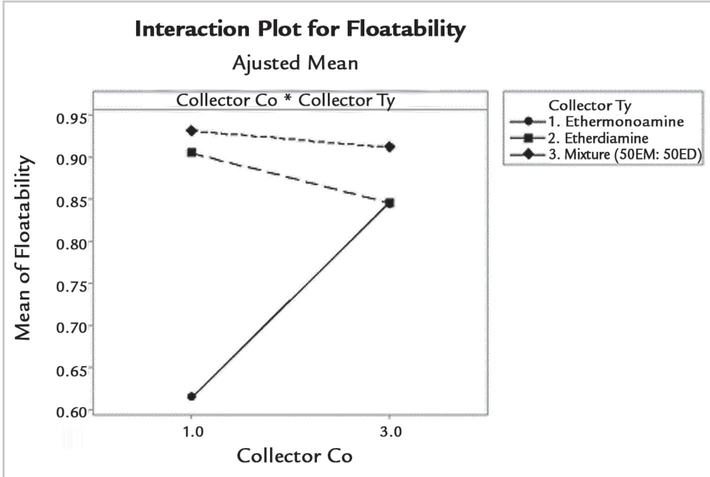

Figure 4 - Plot of the adjusted means interaction for floatability.

This effect can be explained as a possible formation of hemi-micelle. Cationic amine species adsorb on the quartz surface by an electrostatic attraction mechanism and immobilization by formation of hemimicelles as proposed by Fuerstenau and Palmer (1975) and still presently accepted (Baltar, 2021). Studies by Zhang and Somasundaran (2006), Huang *et al.* (2014) and Fan *et al.* (2020) reported that increasing in collector concentration possibly causes the formation of a complete bilayer resulting in a surfactant concentration close to or equal to the critical hemimicelle concentration (CHC), thus reversal in the charge of the mineral surface occurs, rendering it hydrophilic again and consequently decreasing the mineral floatability. This effect was not observed for ethermonoamine in the evaluated concentrations.

Effect of etheramines and their mixture in depressant presence

Since the iron ore reverse cationic flotation requires the use of starch as hematite depressant (Rath and Sahoo, 2020), tests in cassava starch presence were performed to check the influence of depressant on the collector action. Figure 5 shows that cassava starch addition significantly inhibits the quartz floatability (Matos, 2017). The average results indicated that 5mg/L of starch reduced 70% of quartz floatability.

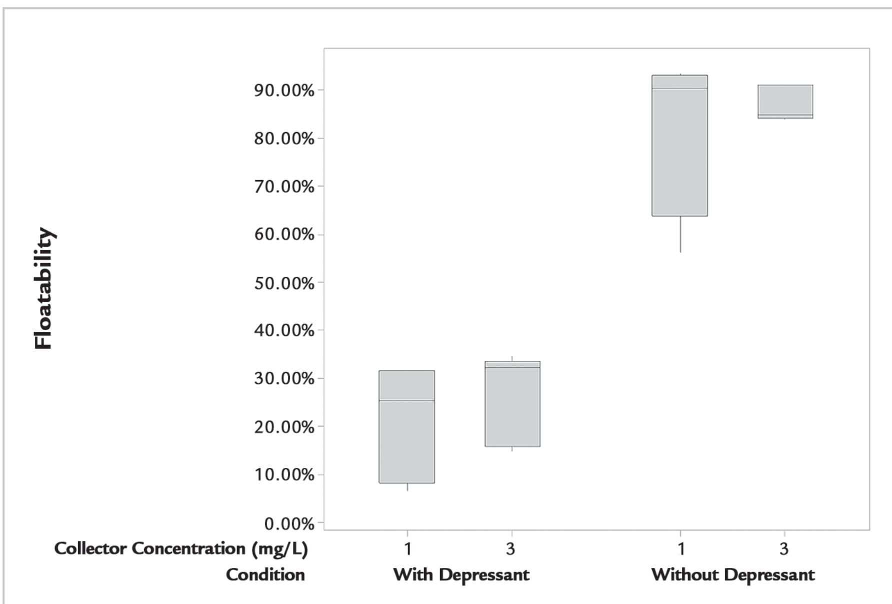

Figure 5 - Boxplot of quartz floatability.

The results presented in Figure 6 indicate higher quartz floatability at 3mg/L than at 1mg/L for both etheramines and for the mixture, elucidating that the collector-depressant interaction has inhibited hemimicelle formation. Unlike the results previously presented in the absence of a depressant, etherdiamine showed lower floatability than ethermonoamine. The binary mixture 1:1, in turn, had an additive effect.

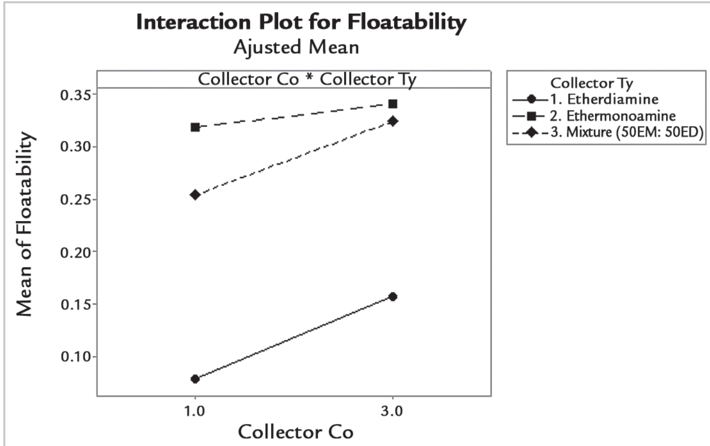

Figure 6 - Plot of main effects of the adjusted means for floatability.

Bench scale Flotation

Table 3 presents the Design of Experiments and the found results of bench scale flotation. These results are shown and discussed at next graphics, by statistical analysis.

Table 3 - DOE of bench scale flotation tests and its results.

Collector Type	Collector Dosage (g/t)	%Fec	$\%SiO_2c$	%Fer	Mass Recovery	Iron Recovery	Selective Index
Ethermonoamine	45	66.38	2.46	20.34	61.51	83.91	9.69
Ethermonoamine	45	66.52	2.36	20.37	61.12	83.70	9.87
Mixture 1:1	45	66.88	2.26	18.75	62.11	85.40	10.64
Mixture 1:1	45	66.55	2.20	19.35	62.25	85.01	10.63
Etherdiamine	45	66.37	2.81	14.72	64.91	89.29	11.19
Etherdiamine	45	66.11	3.14	13.20	66.80	90.97	11.32
Ethermonoamine	55	66.27	2.17	18.64	57.16	82.59	11.02
Ethermonoamine	55	66.38	2.06	18.35	57.48	83.02	11.43
Mixture 1:1	55	66.69	1.88	17.34	58.07	84.20	12.41
Mixture 1:1	55	66.51	2.08	16.75	58.25	84.71	12.07
Etherdiamine	55	66.43	2.27	15.68	57.16	84.97	12.03
Etherdiamine	55	66.29	2.37	14.24	57.48	86.29	12.52

The previous significance analysis of the tested factors (etheramine dosage and type) and their interaction on the response variables silica content in the concentrate ($\%SiO_2c$), iron metallic recovery and Gaudin's selectivity index (SI) was done by Pareto Chart. The collector dosage and type were significant for all the response variables, and the interaction between them was significant only for metallic iron recovery.

Figure 7 shows $\%SiO_2c$ reduction as a function of collectors' dosage increase for each etheramine type and their binary mixture influence. The ethermonoamine yielded lower silica content than etherdiamine. However, the binary mixture provided an even lower value,

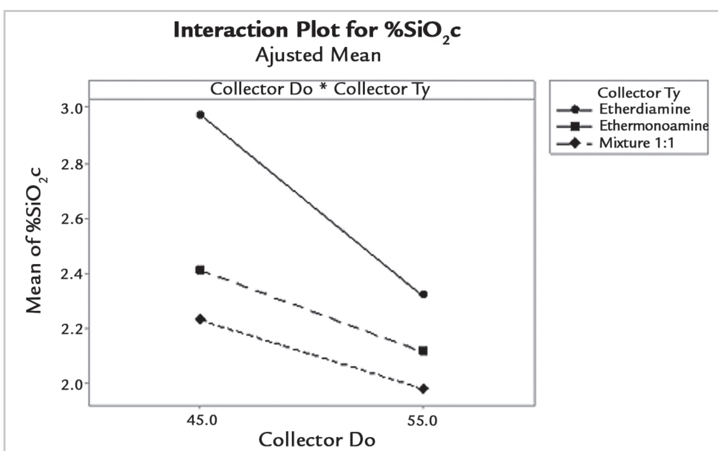

Figure 7 - Plot of main effects of the adjusted means for $\%SiO_2$ in concentrate.

clearly demonstrating the occurrence of the synergistic effect for this parameter.

The results in Figure 8 show the influence of the increasing collector dosage on iron recovery reduction; higher values being achieved by etherdiamine. Thus, the binary mixture presented an intermediate additive effect, since the use of ethermonoamine leads to worse results. According to Matos *et al*., (2021.b), the ethermonoamine is a powerful collector in comparison to etherdiamine, and its lesser iron recovery is a function of the higher entrainment of fine iron particles into the froth.

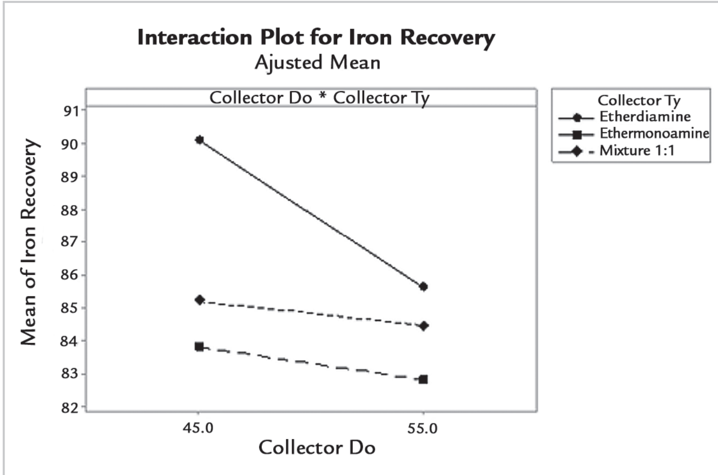

Figure 8 - Plot of main effects of the adjusted means for iron recovery.

Figure 9 presents the effects of dosage and collector type on Gaudin's Selective Index (SI). Etherdiamine showed better selectivity in comparison with ethermonoamine, replicating the results found by Matos 2021(b), at the same tested dosage range. Again, the mixture had an additive effect. At 55g/t dosage, the SI values for pure etherdiamine and binary mixture were coincident, proving the mixture use viability.

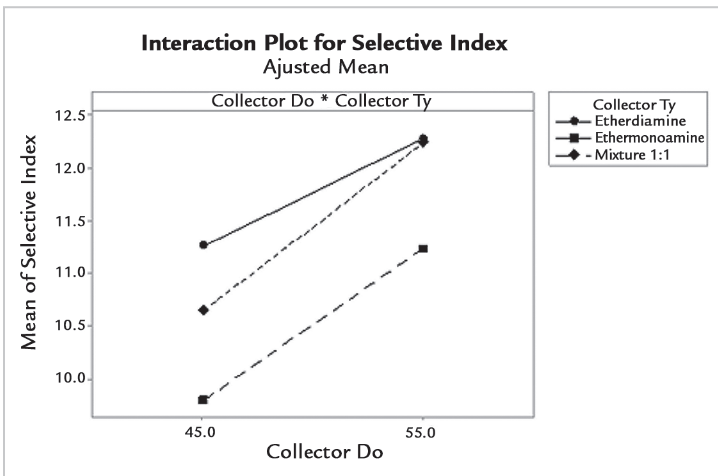

Figure 9 - Plot of main effects of the adjusted means for Selective Index.

4. Conclusions

Collector mixtures impart different effects on quartz floatability and on iron ore reverse cationic flotation performance. These effects can be additive, antagonic and ideally synergistic, depending on tested conditions, such as collector type, concentration or dosage and their interaction. The results of microflotation experiments showed that the binary mixture of ethermonoamine and etherdiamine presented a synergistic effect on quartz floatability in depressant absence. In bench flotation, the synergistic effect was also observed on the concentrate silica content (%SiO_2c), while for iron metallic recovery and Selective Index, the mixture use had an additive effect in comparison with each collector individually.

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